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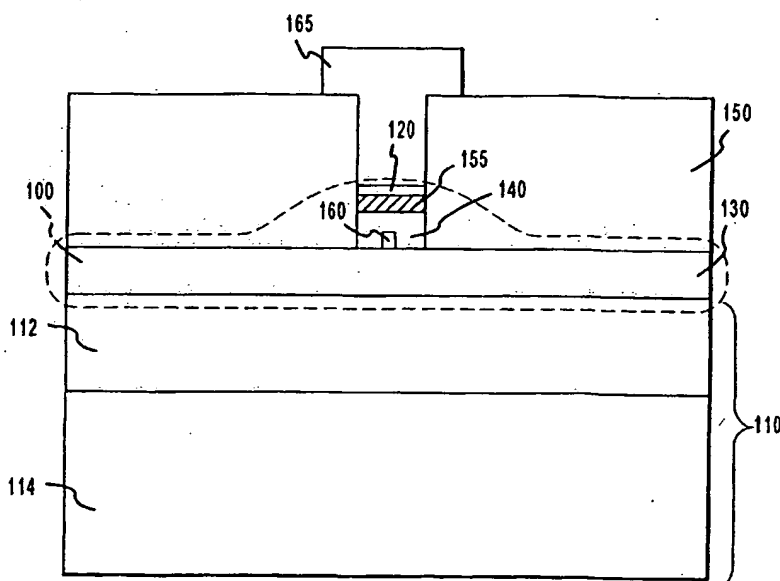
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(54) Title: MICROELECTRONIC PROGRAMMABLE DEVICE AND METHODS OF FORMING AND PROGRAMMING THE SAME



(57) Abstract: A microelectronic programmable structure and methods of forming and programming the structure are disclosed. The programmable structure generally include an ion conductor (140) and a plurality of electrodes (160, 120). Electrical properties of the structure may be altered by applying a bias across the electrodes, and thus information may be stored using the structure.

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**MICROELECTRONIC PROGRAMMABLE DEVICE  
AND METHODS OF FORMING AND PROGRAMMING THE SAME**

**FIELD OF THE INVENTION**

5       The present invention generally relates to microelectronic devices. More particularly, the invention relates to programmable microelectronic structures suitable for use in integrated circuits.

**BACKGROUND OF THE INVENTION**

10       Memory devices are often used in electronic systems and computers to store information in the form of binary data. These memory devices may be characterized into various types, each type having associated with it various advantages and disadvantages.

For example, random access memory ("RAM") which may be found in personal computers is typically volatile semiconductor memory; in other words, the stored data is lost  
15 if the power source is disconnected or removed. Dynamic RAM ("DRAM") is particularly volatile in that it must be "refreshed" (*i.e.*, recharged) every few microseconds in order to maintain the stored data. Static RAM ("SRAM") will hold the data after one writing so long as the power source is maintained; once the power source is disconnected, however, the data is lost. Thus, in these volatile memory configurations, information is only retained so long  
20 as the power to the system is not turned off. In general, these RAM devices can take up significant chip area and therefore may be expensive to manufacture and consume relatively large amounts of energy for data storage. Accordingly, improved memory devices suitable for use in personal computers and the like are desirable.

Other storage devices such as magnetic storage devices (*e.g.*, floppy disks, hard disks  
25 and magnetic tape) as well as other systems, such as optical disks, CD-RW and DVD-RW are non-volatile, have extremely high capacity, and can be rewritten many times. Unfortunately, these memory devices are physically large, are shock/vibration-sensitive, require expensive mechanical drives, and may consume relatively large amounts of power. These negative aspects make such memory devices non-ideal for low power portable  
30 applications such as lap-top and palm-top computers, personal digital assistants ("PDAs"), and the like.

Due, at least in part, to a rapidly growing numbers of compact, low-power portable computer systems in which stored information changes regularly, low energy read/write

semiconductor memories have become increasingly desirable and widespread. Furthermore, because these portable systems often require data storage when the power is turned off, non-volatile storage devices are desired for use in such systems.

5 One type of programmable semiconductor non-volatile memory device suitable for use in such systems is a programmable read-only memory ("PROM") device. One type of PROM, a write-once read-many ("WORM") device, uses an array of fusible links. Once programmed, the WORM device cannot be reprogrammed.

10 Other forms of PROM devices include erasable PROM ("EPROM") and electrically erasable PROM (EEPROM) devices, which are alterable after an initial programming. EPROM devices generally require an erase step involving exposure to ultra violet light prior to programming the device. Thus, such devices are generally not well suited for use in portable electronic devices. EEPROM devices are generally easier to program, but suffer from other deficiencies. In particular, EEPROM devices are relatively complex, are relatively difficult to manufacture, and are relatively large. Furthermore, a circuit including  
15 EEPROM devices must withstand the high voltages necessary to program the device. Consequently, EEPROM cost per bit of memory capacity is extremely high compared with other means of data storage. Another disadvantage of EEPROM devices is that, although they can retain data without having the power source connected, they require relatively large amounts of power to program. This power drain can be considerable in a compact portable  
20 system powered by a battery.

In view of the various problems associated with conventional data storage devices described above, a relatively non-volatile, programmable device which is relatively simple and inexpensive to produce is desired. Furthermore, this memory technology should meet the requirements of the new generation of portable computer devices by operating at a  
25 relatively low voltage while providing high storage density and a low manufacturing cost.

#### SUMMARY OF THE INVENTION

The present invention provides improved microelectronic devices for use in integrated circuits. More particularly, the invention provides relatively non-volatile,  
30 programmable devices suitable for memory and other integrated circuits.

The ways in which the present invention addresses various drawbacks of now-known programmable devices are discussed in greater detail below. However, in general, the

present invention provides a programmable device that is relatively easy and inexpensive to manufacture, and which is relatively easy to program.

In accordance with one exemplary embodiment of the present invention, a programmable structure includes an ion conductor and at least two electrodes. The structure is configured such that when a bias is applied across two electrodes, one or more electrical properties of the structure change. In accordance with one aspect of this embodiment, a resistance across the structure changes when a bias is applied across the electrodes. In accordance with other aspects of this embodiment, a capacitance or other electrical property of the structure changes upon application of a bias across the electrodes. One or more of these electrical changes may suitably be detected. Thus, stored information may be retrieved from a circuit including the structure.

In accordance with another exemplary embodiment of the invention, a programmable structure includes an ion conductor, at least two electrodes, and a barrier interposed between at least a portion of one of the electrodes and the ion conductor. In accordance with one aspect of this embodiment the barrier material includes a material configured to reduce diffusion of ions between the ion conductor and at least one electrode. The diffusion barrier may also serve to prevent undesired electrodeposition growth within a portion of the structure. In accordance with another aspect, the barrier material includes an insulating material. Inclusion of an insulating material increases the voltage required to reduce the resistance of the device. In accordance with yet another aspect of this embodiment, the barrier includes material that conducts ions, but which is relatively resistant to the conduction of electrons. Use of such material may reduce undesired plating at an electrode and increase the thermal stability of the device.

In accordance with another exemplary embodiment of the invention, a programmable microelectronic structure is formed on a surface of a substrate by forming a first electrode on the substrate, depositing a layer of ion conductor material over the first electrode, and depositing conductive material onto the ion conductor material. In accordance with one aspect of this embodiment, a solid solution including the ion conductor and excess conductive material is formed by dissolving (e.g., via thermal and/or photodissolution) a portion of the conductive material in the ion conductor. In accordance with a further aspect, only a portion of the conductive material is dissolved, such that a portion of the conductive material remains on a surface of the ion conductor to form an electrode on a surface of the ion conductor material.

In accordance with another embodiment of the present invention, at least a portion of a programmable structure is formed within a through-hole or via in an insulating material. In accordance with one aspect of this embodiment, a first electrode feature is formed on a surface of a substrate, insulating material is deposited onto a surface of the electrode feature, a via is formed within the insulating material, and a portion of the programmable structure is formed within the via. After the via is formed within the insulating material, a portion of the structure within the via is formed by depositing an ion conductive material onto the conductive material, depositing a second electrode material onto the ion conductive material, and, if desired, removing any excess electrode, ion conductor, and/or insulating material. In accordance with another aspect of this embodiment, only the ion conductor is formed within the via. In this case, a first electrode is formed below the insulating material and in contact with the ion conductor and the second electrode is formed above the insulating material and in contact with the ion conductor. The configuration of the via may be changed to alter (e.g., reduce) a contact area between one or more of the electrodes and the ion conductor. Reducing the cross-sectional area of the interface between the ion conductor and the electrode increases the efficiency of the device (change in electrical property per amount of power supplied to the device). In accordance with another aspect of this embodiment, the via may extend through the lower electrode to reduce the interface area between the electrode and the ion conductor. In accordance with yet another aspect of this embodiment, a portion of the ion conductor may be removed from the via or the ion conductor material may be directionally deposited into only a portion of the via to further reduce an interface between an electrode and the ion conductor.

In accordance with another embodiment of the invention, a programmable device may be formed on a surface of a substrate.

In accordance with a further exemplary embodiment of the invention, multiple bits of information are stored in a single programmable structure. In accordance with one aspect of this embodiment, a programmable structure includes a floating electrode interposed between two additional electrodes.

In accordance with yet another embodiment of the invention, multiple programmable devices are coupled together using a common electrode (e.g., a common anode or a common cathode).

In accordance with yet another embodiment of the invention, multiple programmable devices share a common electrode.

In accordance with yet a further exemplary embodiment of the present invention, a capacitance of a programmable structure is altered by causing ions within an ion conductor of the structure to migrate.

5

#### BRIEF DESCRIPTION OF THE DRAWINGS

A more complete understanding of the present invention may be derived by referring to the detailed description and claims, considered in connection with the figures, wherein like reference numbers refer to similar elements throughout the figures, and:

10 Figure 1 is a cross-sectional illustration of a programmable structure formed on a surface of a substrate in accordance with the present invention;

Figure 2 is a cross-sectional illustration of a programmable structure in accordance with an alternative embodiment of the present invention;

Figure 3 is a current-voltage diagram illustrating current and voltage characteristics of the device illustrated in Figure 2 in an "on" and "off" state;

15 Figure 4 is a cross-sectional illustration of a programmable structure in accordance with yet another embodiment of the present invention;

Figure 5 is a schematic illustration of a portion of a memory device in accordance with an exemplary embodiment of the present invention;

20 Figure 6 is a schematic illustration of a portion of a memory device in accordance with an alternative embodiment of the present invention;

Figures 7 and 8 are a cross-sectional illustrations of a programmable structure having an ion conductor/electrode contact interface formed about a perimeter of the ion conductor in accordance with another embodiment of the present invention;

25 Figures 9 and 10 are a cross-sectional illustrations of a programmable structure having an ion conductor/electrode contact interface formed about a perimeter of the ion conductor in accordance with yet another embodiment of the present invention;

Figures 11 and 12 illustrate a programmable device having a horizontal configuration in accordance with the present invention;

30 Figures 13-19 illustrate programmable device structures with reduced electrode/ion conductor interface surface area in accordance with the present invention;

Figure 20 illustrates a programmable device with a tapered ion conductor in accordance with the present invention;

Figures 21-24 illustrate a programmable device including a floating electrode in accordance with the present invention; and

Figures 25-29 illustrate common electrode programmable device structures in accordance with the present invention.

5 Skilled artisans will appreciate that elements in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the elements in the figures may be exaggerated relative to other elements to help to improve understanding of embodiments of the present invention.

#### 10 DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

The present invention generally relates to microelectronic devices. More particularly, the invention relates to programmable structures or devices suitable for various integrated circuit applications.

15 Figures 1 and 2 illustrate programmable microelectronic structures 100 and 200 formed on a surface of a substrate 110 in accordance with an exemplary embodiment of the present invention. Structures 100 and 200 include electrodes 120 and 130, an ion conductor 140, and optionally include buffer or barrier layers 155 and/or 255.

20 Generally, structures 100 and 200 are configured such that when a bias greater than a threshold voltage ( $V_T$ ), discussed in more detail below, is applied across electrodes 120 and 130, the electrical properties of structure 100 change. For example, in accordance with one embodiment of the invention, as a voltage  $V \geq V_T$  is applied across electrodes 120 and 130, conductive ions within ion conductor 140 begin to migrate and form an electrodeposit (e.g., electrodeposit 160) at or near the more negative of electrodes 120 and 130; such an electrodeposit, however, is not required to practice the present invention. The term  
25 "electrodeposit" as used herein means any area within the ion conductor that has an increased concentration of reduced metal or other conductive material compared to the concentration of such material in the bulk ion conductor material. As the electrodeposit forms, the resistance between electrodes 120 and 130 decreases, and other electrical properties may also change. In the absence of any insulating barriers, which are discussed in  
30 more detail below, the threshold voltage required to grow the electrodeposit from one electrode toward the other and thereby significantly reduce the resistance of the device is approximately the redox potential of the system, typically a few hundred millivolts. If the same voltage is applied in reverse, the electrodeposit will dissolve back into the ion



conductor and the device will return to a high resistance state. In accordance with other embodiments of the invention, application of an electric field between electrodes 120 and 130 may cause ions dissolved within conductor 140 to migrate and thus cause a change in the electrical properties of device 100, without the formation of an electrodeposit. Structures 5 100 and 200 may be used to store information and thus may be used in memory circuits. For example, structure 100 or other programmable structures in accordance with the present invention may suitably be used in memory devices to replace DRAM, SRAM, PROM, EPROM, or EEPROM devices. In addition, programmable structures of the present invention may be used for other applications where programming or changing of electrical 10 properties of a portion of an electrical circuit are desired.

Substrate 110 may include any suitable material. For example, substrate 110 may include semiconductive, conductive, semiinsulative, insulative material, or any combination of such materials. In accordance with one embodiment of the invention, substrate 110 includes an insulating material 112 and a portion 114 including microelectronic devices 15 formed on a semiconductor substrate. Layers 112 and 114 may be separated by additional layers (not shown) such as, for example, layers typically used to form integrated circuits. Because the programmable structures can be formed over insulating or other materials, the programmable structures of the present invention are particularly well suited for applications where substrate (e.g., semiconductor material) space is a premium.

20 Electrodes 120 and 130 may be formed of any suitable conductive material. For example, electrodes 120 and 130 may be formed of doped polysilicon material or metal.

In accordance with one exemplary embodiment of the invention, one of electrodes 120 and 130 is formed of a material including a metal that dissolves in ion conductor 140 when a sufficient bias ( $V \geq V_T$ ) is applied across the electrodes (oxidizable electrode) and 25 the other electrode is relatively inert and does not dissolve during operation of the programmable device (an indifferent electrode). For example, electrode 120 may be an anode during a write process and be comprised of a material including silver that dissolves in ion conductor 140 and electrode 130 may be a cathode during the write process and be comprised of an inert material such as tungsten, nickel, molybdenum, platinum, metal silicides, and the like. Having at least one electrode formed of a material including a metal 30 which dissolves in ion conductor 140 facilitates maintaining a desired dissolved metal concentration within ion conductor 140, which in turn facilitates rapid and stable electrodeposit 160 formation within ion conductor 140 or other electrical property change

during use of structure 100 and/or 200. Furthermore, use of an inert material for the other electrode (cathode during a write operation) facilitates electrodisolution of any electrodeposit that may have formed and/or return of the programmable device to an erased state after application of a sufficient voltage.

5 During an erase operation, dissolution of any electrodeposit that may have formed preferably begins at or near the oxidizable electrode/electrodeposit interface. Initial dissolution of the electrodeposit at the oxidizable electrode/electrodeposit interface may be facilitated by forming structure 100 such that the resistance of the at the oxidizable  
10 electrode/electrodeposit interface is greater than the resistance at any other point along the electrodeposit, particularly, the interface between the electrodeposit and the indifferent electrode.

One way to achieve relatively low resistance at the indifferent electrode is to form the electrode of relatively inert, non-oxidizing material such as platinum. Use of such material reduces formation of oxides at the interface between ion conductor 140 and the indifferent  
15 electrode as well as the formation of compounds or mixtures of the electrode material and ion conductor 140 material, which typically have a higher resistance than ion conductor 140 or the electrode material.

Relatively low resistance at the indifferent electrode may also be obtained by forming a barrier layer between the oxidizable electrode (anode during a write operation),  
20 wherein the barrier layer is formed of material having a relatively high resistance. Exemplary high resistance materials include layers (e.g., layer 155 and/or layer 255) of ion conducting material (e.g.,  $\text{Ag}_x\text{O}$ ,  $\text{Ag}_x\text{S}$ ,  $\text{Ag}_x\text{Se}$ ,  $\text{Ag}_x\text{Te}$ , where  $x \geq 2$ ,  $\text{Ag}_y\text{I}$ , where  $x \geq 1$ ,  $\text{CuI}_2$ ,  $\text{CuO}$ ,  $\text{CuS}$ ,  $\text{CuSe}$ ,  $\text{CuTe}$ ,  $\text{GeO}_2$ , or  $\text{SiO}_2$ ) interposed between ion conductor 140 and a metal layer such as silver. Some of these materials have additional benefits as discussed in  
25 more detail below.

Reliable growth and dissolution of an electrodeposit can also be facilitated by providing a roughened indifferent electrode surface (e.g., a root mean square roughness of greater than about 1 nm) at the electrode/ion conductor interface. The roughened surface may be formed by manipulating film deposition parameters and/or by etching a portion of  
30 one of the electrode of ion conductor surfaces. During a write operation, relatively high electrical fields form about the spikes or peaks of the roughened surface, and thus the electrodeposits are more likely to form about the spikes or peaks. As a result, more reliable and uniform changes in electrical properties for an applied voltage across electrodes 120 and

130 may be obtained by providing a roughed interface between the indifferent electrode (cathode during a write operation) and ion conductor 140.

Oxidizable electrode material may have a tendency to thermally dissolve or diffuse into ion conductor 140, particularly during fabrication and/or operation of structure 100.

5 The thermal diffusion is undesired because it may reduce the resistance of structure 100 and thus reduce the change of an electrical property during use of structure 100.

To reduce undesired diffusion of oxidizable electrode material into ion conductor 140 and in accordance with another embodiment of the invention, the oxidizable electrode includes a metal intercalated in a transition metal sulfide or selenide material such as  $A_x(MB_2)_{1-x}$ , where A is Ag or Cu, B is S or Se, M is a transition metal such as Ta, V, and Ti, and x ranges from about 0.1 to about 0.7. The intercalated material mitigates undesired thermal diffusion of the metal (Ag or Cu) into the ion conductor material, while allowing the metal to participate in the electrodeposit growth upon application of a sufficient voltage across electrodes 120 and 130. For example, when silver is intercalated into a TaS<sub>2</sub> film, the TaS<sub>2</sub> film can include up to about 66.8 atomic percent silver. The  $A_x(MB_2)_{1-x}$  material is preferably amorphous to prevent to prevent undesired diffusion of the metal through the material. The amorphous material may be formed by, for example, physical vapor deposition of a target material comprising  $A_x(MB_2)_{1-x}$ .

$\alpha$ -AgI is another suitable material for the oxidizable electrode, as well as the indifferent electrode. Similar to the  $A_x(MB_2)_{1-x}$  material discussed above,  $\alpha$ -AgI can serve as a source of Ag during operation of structure 100—e.g., upon application of a sufficient bias, but the silver in the AgI material does not readily thermally diffuse into ion conductor 140. AgI has a relatively low activation energy for conduction of electricity and does not require doping to achieve relatively high conductivity. When the oxidizable electrode is formed of AgI, depletion of silver in the AgI layer may arise during operation of structure 100, unless excess silver is provided to the electrode. One way to provide the excess silver is to form a silver layer adjacent the AgI layer as discussed above when AgI is used as a buffer layer. The AgI layer (e.g., layer 155 and/or 255) reduces thermal diffusion of Ag into ion conductor 140, but does not significantly affect conduction of Ag during operation of structure 100. In addition, use of AgI increases the operational efficiency of structure 100 because the AgI mitigates non-Faradaic conduction (conduction of electrons that do not participate in the electrochemical reaction).

Other materials suitable for buffer layers 155 and/or 255 include  $\text{GeO}_2$  and  $\text{SiO}_x$ . Amorphous  $\text{GeO}_2$  is relatively porous and will "soak up" silver during operation of device 100, but will retard the thermal diffusion of silver to ion conductor 140, compared to structures or devices that do not include a buffer layer. When ion conductor 140 includes germanium,  $\text{GeO}_2$  may be formed by exposing ion conductor 140 to an oxidizing environment at a temperature of about 300 °C to about 800 °C or by exposing ion conductor 140 to an oxidizing environment in the presence of radiation having an energy greater than the band gap of the ion conductor material. The  $\text{GeO}_2$  may also be deposited using physical vapor deposition (from a  $\text{GeO}_2$  target) or chemical vapor deposition (from  $\text{GeH}_4$  and an  $\text{O}_2$ ).

Buffer layers can also be used to increase a "write voltage" by placing the buffer layer (e.g.,  $\text{GeO}_2$  or  $\text{SiO}_x$ ) between ion conductor 140 and the indifferent electrode. The buffer material allows metal such as silver to diffuse through the buffer and take part in the electrochemical reaction.

In accordance with one embodiment of the invention, at least one electrode 120 and 130 is formed of material suitable for use as an interconnect metal. For example, electrode 130 may form part of an interconnect structure within a semiconductor integrated circuit. In accordance with one aspect of this embodiment, electrode 130 is formed of a material that is substantially insoluble in material comprising ion conductor 140. Exemplary materials suitable for both interconnect and electrode 130 material include metals and compounds such as tungsten, nickel, molybdenum, platinum, metal silicides, and the like.

Layers 155 and/or 255 may also include a material that restricts migration of ions between conductor 140 and the electrodes. In accordance with exemplary embodiments of the invention, a barrier layer includes conducting material such as titanium nitride, titanium tungsten, a combination thereof, or the like. The barrier may be electrically indifferent, i.e., it allows conduction of electrons through structure 100 or 200, but it does not itself contribute ions to conduction through structure 200. An electrically indifferent barrier may reduce undesired dendrite growth during operation of the programmable device, and thus may facilitate an "erase" or dissolution of electrodeposit 160 when a bias is applied which is opposite to that used to grow the electrodeposit. In addition, use of a conducting barrier allows for the "indifferent" electrode to be formed of oxidizable material because the barrier prevents diffusion of the electrode material to the ion conductor.

Ion conductor 140 is formed of material that conducts ions upon application of a sufficient voltage. Suitable materials for ion conductor 140 include glasses and

semiconductor materials. In one exemplary embodiment of the invention, ion conductor 140 is formed of chalcogenide material.

Ion conductor 140 may also suitably include dissolved conductive material. For example, ion conductor 140 may comprise a solid solution that includes dissolved metals and/or metal ions. In accordance with one exemplary embodiment of the invention, conductor 140 includes metal and/or metal ions dissolved in chalcogenide glass. An exemplary chalcogenide glass with dissolved metal in accordance with the present invention includes a solid solution of  $As_xS_{1-x}Ag$ ,  $Ge_xSe_{1-x}Ag$ ,  $Ge_xS_{1-x}Ag$ ,  $As_xS_{1-x}Cu$ ,  $Ge_xSe_{1-x}Cu$ ,  $Ge_xS_{1-x}Cu$ , where  $x$  ranges from about 0.1 to about 0.5 other chalcogenide materials including silver, copper, zinc, combinations of these materials, and the like. In addition, conductor 140 may include network modifiers that affects mobility of ions through conductor 140. For example, materials such as metals (e.g., silver), halogens, halides, or hydrogen may be added to conductor 140 to enhance ion mobility and thus increase erase/write speeds of the structure.

A solid solution suitable for use as ion conductor 140 may be formed in a variety of ways. For example, the solid solution may be formed by depositing a layer of conductive material such as metal over an ion conductive material such as chalcogenide glass and exposing the metal and glass to thermal and/or photo dissolution processing. In accordance with one exemplary embodiment of the invention, a solid solution of  $As_2S_3-Ag$  is formed by depositing  $As_2S_3$  onto a substrate, depositing a thin film of  $Ag$  onto the  $As_2S_3$ , and exposing the films to light having energy greater than the optical gap of the  $As_2S_3$ ,—e.g., light having a wavelength of less than about 500 nanometers. If desired, network modifiers may be added to conductor 140 during deposition of conductor 140 (e.g., the modifier is in the deposited material or present during conductor 140 material deposition) or after conductor 140 material is deposited (e.g., by exposing conductor 140 to an atmosphere including the network modifier).

In accordance with another embodiment of the invention, a solid solution may be formed by depositing one of the constituents onto a substrate or another material layer and reacting the first constituent with a second constituent. For example, germanium (preferably amorphous) may be deposited onto a portion of a substrate and the germanium may be reacted with  $H_2Se$  to form a Ge-Se glass. Similarly, As can be deposited and reacted with the  $H_2Se$  gas, or arsenic or germanium can be deposited and reacted with  $H_2S$  gas. Silver or other metal can then be added to the glass as described above.

In accordance with one aspect of this embodiment, a solid solution ion conductor 140 is formed by depositing sufficient metal onto an ion conductor material such that a portion of the metal can be dissolved within the ion conductor material and a portion of the metal remains on a surface of the ion conductor to form an electrode (e.g., electrode 120). In accordance with alternative embodiments of the invention, solid solutions containing dissolved metals may be directly deposited onto substrate 110 and the electrode then formed overlying the ion conductor.

An amount of conductive material such as metal dissolved in an ion conducting material such as chalcogenide may depend on several factors such as an amount of metal available for dissolution and an amount of energy applied during the dissolution process. However, when a sufficient amount of metal and energy are available for dissolution in chalcogenide material using photodissolution, the dissolution process is thought to be self limiting, substantially halting when the metal cations have been reduced to their lowest oxidation state. In the case of  $\text{As}_2\text{S}_3$ -Ag, this occurs at  $\text{Ag}_4\text{As}_2\text{S}_3 = 2\text{Ag}_2\text{S} + \text{As}_2\text{S}_3$ , having a silver concentration of about 44 atomic percent. If, on the other hand, the metal is dissolved in the chalcogenide material using thermal dissolution, a higher atomic percentage of metal in the solid solution may be obtained, provided a sufficient amount of metal is available for dissolution.

In accordance with a further embodiment of the invention, the solid solution is formed by photodissolution to form a macrohomogeneous ternary compound and additional metal is added to the solution using thermal diffusion (e.g., in an inert environment at a temperature of about 85 °C to about 150 °C) to form a solid solution containing, for example, about 30 to about 50, and preferably about 34 atomic percent silver. Ion conductors having a metal concentration above the photodissolution solubility level facilitates formation of electrodeposits that are thermally stable at operating temperatures (typically about 85 °C to about 150 °C) of devices 100 and 200. Alternatively, the solid solution may be formed by thermally dissolving the metal into the ion conductor at the temperature noted above; however, solid solutions formed exclusively from photodissolution are thought to be less homogeneous than films having similar metal concentrations formed using photodissolution and thermal dissolution.

Ion conductor 140 may also include a filler material, which fills interstices or voids. Suitable filler materials include non-oxidizable and non-silver based materials such as a non-conducting, immiscible silicon oxide and/or silicon nitride, having a cross-sectional

dimension of less than about 1 nm, which do not contribute to the growth of an electrodeposit. In this case, the filler material is present in the ion conductor at a volume percent of up to about 5 percent to reduce a likelihood that an electrodeposit will spontaneously dissolve into the supporting ternary material as the device is exposed to elevated temperature, which leads to more stable device operation without compromising the performance of the device. Ion conductor 140 may also include filler material to reduce an effective cross-sectional area of the ion conductor. In this case, the concentration of the filler material, which may be the same filler material described above but having a cross-sectional dimension up to about 50 nm, is present in the ion conductor material at a concentration of up to about 50 percent by volume. The filler material may also include metal such as silver or copper to fill the voids in the ion conductor material.

In accordance with one exemplary embodiment of the invention, ion conductor 140 includes a germanium-selenide glass with silver diffused in the glass. Germanium selenide materials are typically formed from selenium and  $\text{Ge}(\text{Se})_{4/2}$  tetrahedra that may combine in a variety of ways. In a Se-rich region, Ge is 4-fold coordinated and Se is 2-fold coordinated, which means that a glass composition near  $\text{Ge}_{0.20}\text{Se}_{0.80}$  will have a mean coordination number of about 2.4. Glass with this coordination number is considered by constraint counting theory to be optimally constrained and hence very stable with respect to devitrification. The network in such a glass is known to self-organize and become stress-free, making it easy for any additive, e.g., silver, to finely disperse and form a mixed-glass solid solution. Accordingly, in accordance with one embodiment of the invention, ion conductor 140 includes a glass having a composition of  $\text{Ge}_{0.17}\text{Se}_{0.83}$  to  $\text{Ge}_{0.25}\text{Se}_{0.75}$ .

The composition and structure of ion conductor 140 material often depends on the starting or target material used to form the conductor. Generally, it is desired to form a homogenous material layer for conductor 140 to facilitate reliable and repeatable device performance. In accordance with one embodiment of the invention, a target for physical vapor deposition of material suitable for ion conductor 140 is formed by selecting a proper ampoule, preparing the ampoule, maintaining proper temperatures during formation of the glass, slow rocking the composition, and quenching the composition.

Volume and wall thickness are important factors for consideration in selecting an ampoule for forming glass. The wall thickness must be thick enough to withstand gas pressures that arise during the glass formation process and are preferably thin enough to facilitate heat exchange during the formation process. In accordance with exemplary

embodiment of the invention, quartz ampoules with a wall thickness of about 1 mm are used to form Se and Te based chalcogenide glasses, whereas quartz ampoules with a wall thickness of about 1.5 mm are used to form sulfur-based chalcogenide glasses. In addition, the volume of the ampoule is preferably selected such that the volume of the ampoule is about five times greater than the liquid glass precursor material.

Once the ampoule is selected, the ampoule is prepared for glass formation, in accordance with one embodiment of the invention, by cleaning the ampoule with hydrofluoric acid, ethanol and acetone, drying the ampoule for at least 24 hours at about 120 °C, evacuating the ampoule and heating the ampoule until the ampoule turns a cherry red color and cooling the ampoule under vacuum, filling ampoule with charge and evacuating the ampoule, heating the ampoule while avoiding melting of the constituents to desorb any remaining oxygen, and sealing the ampoule. This process reduces oxygen contamination, which in turn promotes macrohomogeneous growth of the glass.

The melting temperature of the glass formation process depends on the glass material. In the case of germanium-based glasses, sufficient time for the chalcogen to react at low temperature with all available germanium is desired to avoid explosion at subsequent elevated temperatures (the vapor pressure of Se at 920 °C is 10 ATM. and 20 ATM. for S at 720°C). To reduce the risk of explosion, the glass formation process begins by ramping the ampoule temperature to about 300 °C for selenium-based glasses (about 200 °C for sulfur-based glasses) over the period of about an hour and maintaining this temperature for about 12 hours. Next, the temperature is elevated slowly (about 0.5 °C/min) up to a temperature about 50 °C higher than the liquidus temperature of the material and the ampoule remains at about this temperature for about 12 hours. The temperature is then elevated to about 940 °C to ensure melting of all non-reacted germanium for Se-based glasses or about 700 °C for S-based glasses. The ampoule should remain at this elevated temperature for about 24 hours.

The melted glass composition is preferably slow rocked at a rate of about 20/minute at least about six hours to increase the homogeneity of the glass.

Quenching is preferably performed from a temperature at which the vapors and the liquid are in an equilibrium to produce vitrification of the desired composition. In this case, the quenching temperature is about 50 °C over the liquidus temperature of the glass material. Chalcogenide-rich glasses include a range of concentrations in which under-constrained and over-constrained glasses exist. In cases where the glass composition coordinated number is far from the optimal coordination (e.g., coordination numbers of about 2.4 for Ge-Se



systems) the quenching rate has to be fast enough in order to ensure vitrification, e.g., quenching in ice-water or an even stronger coolant such as a mixture of urea and ice-water. In the case of optimally coordinated glasses, quenching can be performed in air at about 25 °C.

5 In accordance with one exemplary embodiment of the invention, at least a portion of structure 100 is formed within a via of an insulating material 150. Forming a portion of structure 100 within a via of an insulating material 150 may be desirable because, among other reasons, such formation allows relatively small structures, e.g., on the order of 10 nanometers, to be formed. In addition, insulating material 150 facilitates isolating various  
10 structures 100 from other electrical components.

Insulating material 150 suitably includes material that prevents undesired diffusion of electrons and/or ions from structure 100. In accordance with one embodiment of the invention, material 150 includes silicon nitride, silicon oxynitride, polymeric materials such as polyimide or parylene, or any combination thereof.

15 A contact 165 may suitably be electrically coupled to one or more electrodes 120, 130 to facilitate forming electrical contact to the respective electrode. Contact 165 may be formed of any conductive material and is preferably formed of a metal such as aluminum, aluminum alloys, tungsten, or copper.

In accordance with one embodiment of the invention, structure 100 is formed by  
20 forming electrode 130 on substrate 110. Electrode 130 may be formed using any suitable method such as, for example, depositing a layer of electrode 130 material, patterning the electrode material, and etching the material to form electrode 130. Insulating layer 150 may be formed by depositing insulating material onto electrode 130 and substrate 110 and forming vias in the insulating material using appropriate patterning and etching processes.  
25 Ion conductor 140 and electrode 120 may then be formed within insulating layer 150 by depositing ion conductor 140 material and electrode 120 material within the via. Such ion conductor and electrode material deposition may be selective - i.e., the material is substantially deposited only within the via, or the deposition processes may be relatively non-selective. If one or more non-selective deposition methods are used, any excess  
30 material remaining on a surface of insulating layer 150 may be removed using, for example, chemical mechanical polishing and/or etching techniques. Barrier layers 155 and/or 255 may similarly be formed using any suitable deposition and/or etch processes.

Information may be stored using programmable structures of the present invention by manipulating one or more electrical properties of the structures. For example, a resistance of a structure may be changed from a "0" or off state to a "1" or on state during a suitable write operation. Similarly, the device may be changed from a "1" state to a "0" state during an erase operation. In addition, as discussed in more detail below, the structure may have multiple programmable states such that multiple bits of information are stored in a single structure.

#### WRITE OPERATION

Figure 3 illustrates current-voltage characteristics of a programmable structure (e.g. structure 200) in accordance with the present invention. In the illustrated embodiment, via diameter,  $D$ , is about 4 microns, conductor 140 is about 35 nanometers thick and formed of  $\text{Ge}_3\text{Se}_7\text{-Ag}$  (near  $\text{As}_8\text{Ge}_3\text{Se}_7$ ), electrode 130 is indifferent and formed of nickel, electrode 120 is formed of silver, and barrier 255 is a native nickel oxide. As illustrated in Figure 3, current through structure 200 in an off state (curve 310) begins to rise upon application of a bias of over about one volt; however, once a write step has been performed (*i.e.*, an electrodeposit has formed), the resistance through conductor 140 drops significantly (*i.e.*, to about 200 ohms), illustrated by curve 320 in Figure 3. As noted above, when electrode 130 is coupled to a more negative end of a voltage supply, compared to electrode 120, an electrodeposit begins to form near electrode 130 and grow toward electrode 120. An effective threshold voltage (*i.e.*, voltage required to cause growth of the electrodeposit and to break through barrier 255, thereby coupling electrodes 320, 330 together is relatively high because of barrier 255. In particular, a voltage  $V \geq V_T$  must be applied to structure 200 sufficient to cause electrons to tunnel through barrier 255 (when barrier 255 comprises an insulating layer) to form the electrodeposit and to overcome the barrier (e.g., by tunneling through or leakage) and conduct through conductor 140 and at least a portion of barrier 255.

In accordance with alternate embodiments of the invention, where no insulating barrier layer is present, an initial "write" threshold voltage is relatively low because no insulative barrier is formed between, for example, ion conductor 140 and either of the electrodes 120, 130.

## READ OPERATION

A state of the device (e.g., 1 or 0) may be read, without significantly disturbing the state, by, for example, applying a forward or reverse bias of magnitude less than a voltage threshold (about 1.4 V for a structure illustrated in Figure 3) for electrodeposition or by  
5 using a current limit which is less than or equal to the minimum programming current (the current which will produce the highest of the on resistance values). A current limited (to about 1 milliamp) read operation is shown in Figure 3. In this case, the voltage is swept from 0 to about 2 V and the current rises up to the set limit (from 0 to 0.2 V), indicating a low resistance (ohmic/linear current-voltage) "on" state. Another way of performing a non-  
10 disturb read operation is to apply a pulse, with a relatively short duration, which may have a voltage higher than the electrochemical deposition threshold voltage such that no appreciable Faradaic current flows, i.e., nearly all the current goes to polarizing/charging the device and not into the electrodeposition process.

## 15 ERASE OPERATION

A programmable structure (e.g., structure 200) may suitably be erased by reversing a bias applied during a write operation, wherein a magnitude of the applied bias is equal to or greater than the threshold voltage for electrodeposition in the reverse direction. In accordance with an exemplary embodiment of the invention, a sufficient erase voltage  
20 ( $V \geq V_T$ ) is applied to structure 200 for a period of time which depends on the strength of the initial connection but is typically less than about 1 millisecond to return structure 200 to its "off" state having a resistance well in excess of a million ohms. In cases where the programmable structure does not include a barrier between conductor 140 and electrode 120, a threshold voltage for erasing the structure is much lower than a threshold voltage for  
25 writing the structure because, unlike the write operation, the erase operation does not require electron tunneling through a barrier or barrier breakdown.

## CONTROL OF OPERATIONAL PARAMETERS

The concentration of conductive material in the ion conductor can be controlled by  
30 applying a bias across the programmable device. For example, metal such as silver may be taken out of solution by applying a negative voltage in excess of the reduction potential of the conductive material. Conversely, conductive material may be added to the ion conductor (from one of the electrodes) by applying a bias in excess of the oxidation potential of the

material. Thus, for example, if the conductive material concentration is above that desired for a particular device application, the concentration can be reduced by reverse biasing the device to reduce the concentration of the conductive material. Similarly, metal may be added to the solution from the oxidizable electrode by applying a sufficient forward bias.

5 Additionally, it is possible to remove excess metal build up at the indifferent electrode by applying a reverse bias for an extended time or an extended bias over that required to erase the device under normal operating conditions. Control of the conductive material may be accomplished automatically using a suitable microprocessor.

This technique may also be used to form one of the electrodes from material within the ion conductor material. For example, silver from the ion conductor may be plated out to form the oxidizable electrode. This allows the oxidizable electrode to be formed after the device is fully formed and thus mitigates problems associated with conductive material diffusing from the oxidizable electrode during manufacturing of the device.

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As noted above, in accordance with yet another embodiment of the invention, multiple bits of data may be stored within a single programmable structure by controlling an amount of electrodeposit which is formed during a write process. An amount of electrodeposit that forms during a write process depends on a number of coulombs or charge supplied to the structure during the write process, and may be controlled by using a current limit power source. In this case, a resistance of a programmable structure is governed by Equation 1, where  $R_{on}$  is the "on" state resistance,  $V_T$  is the threshold voltage for electrodeposition, and  $I_{LIM}$  is the maximum current allowed to flow during the write operation.

15

20

$$R_{on} = \frac{V_T}{I_{LIM}}$$

Equation 1

25 In practice, the limitation to the amount of information stored in each cell will depend on how stable each of the resistance states is with time. For example, if a structure is with a programmed resistance range of about 3.5 k $\Omega$  and a resistance drift over a specified time for each state is about  $\pm 250 \Omega$ , about 7 equally sized bands of resistance (7 states) could be formed, allowing 3 bits of data to be stored within a single structure. In the limit, for near

zero drift in resistance in a specified time limit, information could be stored as a continuum of states, *i.e.*, in analog form.

A portion of an integrated circuit 402, including a programmable structure 400, configured to provide additional isolation from electronic components is illustrated in Figure 4. In accordance with an exemplary embodiment of the present invention, structure 400 includes electrodes 420 and 430, an ion conductor 440, a contact 460, and an amorphous silicon diode 470, such as a Schottky or p-n junction diode, formed between contact 460 and electrode 420. Rows and columns of programmable structures 400 may be fabricated into a high density configuration to provide extremely large storage densities suitable for memory circuits. In general, the maximum storage density of memory devices is limited by the size and complexity of the column and row decoder circuitry. However, a programmable structure storage stack can be suitably fabricated overlying an integrated circuit with the entire semiconductor chip area dedicated to row/column decode, sense amplifiers, and data management circuitry (not shown) since structure 400 need not use any substrate real estate. In this manner, storage densities of many gigabits per square centimeter can be attained using programmable structures of the present invention. Utilized in this manner, the programmable structure is essentially an additive technology that adds capability and functionality to existing semiconductor integrated circuit technology.

Figure 5 schematically illustrates a portion of a memory device including structure 400 having an isolating p-n junction 470 at an intersection of a bit line 510 and a word line 520 of a memory circuit. Figure 6 illustrates an alternative isolation scheme employing a transistor 610 interposed between an electrode and a contact of a programmable structure located at an intersection of a bit line 610 and a word line 620 of a memory device.

Figures 7-10 illustrate programmable devices in accordance with another embodiment of the invention. The devices illustrated in Figures 7-10 have an electrode (e.g., the cathode during a write process) with a smaller cross sectional area in contact with the ion conductor compared to the devices illustrated in Figures 1-2 and 4. The smaller electrode interface area is thought to increase the efficiency and endurance of the device because an increased percentage of ions in the solid solution are able to take part in the electrodeposition process. Thus any cathode plating from ions that do not participate in the electrodeposition process is reduced.

Figures 7 and 8 illustrate a cross sectional and a top cut-away view of a programmable device 700 including an indifferent electrode 710, an oxidizable electrode

720, and an ion conductor 730 former overlying an insulating layer 740 such as silicon oxide, silicon nitride, or the like.

Structure 700 is formed by depositing an indifferent electrode material layer and an insulating layer 750 overlying insulating layer 740. A via is then formed through layer 750 and electrode material layer 710, using an anisotropic etch process (e.g., reactive ion etching or ion milling) such that the via extends to and/or through a portion of layer 740. The via is then filled with ion conductor material and is suitably doped to form a solid solution as described herein. Any excess ion conductor material is removed from the surface of layer 750 and electrode 730 is formed, for example using a deposition and etch process. In this case, the indifferent electrode (cathode during write process) area in contact with ion conductor 730 is the surface area of electrode 710 about the perimeter of conductor 730, rather than the area underlying the ion conductor, as illustrated in Figures 1-2 and 4.

Figures 9 and 10 illustrate a programmable device 900 having an indifferent electrode 910, an oxidizable electrode 920, an ion conductor 930 and insulating layers 940 and 950 in accordance with yet another embodiment of the invention. Structure 900 is similar to structure 700, except that once a via is formed through layer 750, an isotropic etch process (e.g., chemical or plasma) is employed to form the via through electrode 910, such that a sloped intersection between an ion conductor 930 and electrode 910 is formed.

Figures 11 and 12 illustrate another programmable device 1100, with a reduced electrode/ion conductor interface, in accordance with the present invention. Structure 1100 includes electrodes 1110 and 1120 and an ion conductor 1130, formed on a surface of an insulating material 1140, rather than within a via as discussed above. In this case, the programmable structure is formed by defining an ion conductor 1130 patten on a surface of insulating material 1140 (e.g., using deposition and etch techniques) and forming electrodes 1110 and 1120, such that the electrodes each contact a portion of the ion conductor. In the case of the illustrated embodiment, the electrodes are formed overlying and in contact with both a portion of the ion conductor and the insulating material. Although the thickness of the layers may be varied in accordance with specific applications of the device, in a preferred embodiment of the invention, the thickness of the ion conductor and electrode films is about 1 nm to about 100 nm. Sub-lithographic lateral dimensions of portions of the device may be obtained by overexposing photoresist used to pattern the portions and/or over etching the film layer.

Figure 13 illustrates a device 1300 in accordance with yet another embodiment of the invention. Structure 1300 is similar to the devices illustrated in Figure 7 and 8, except that the cross-sectional area of the ion conductor that is in contact with the electrodes is reduced by filling a portion of a via with non-ion conductor material, rather than etching through an electrode layer.

Structure 1300 includes electrodes 1310 and 1320 and an ion conductor 1330 formed within an insulating layer 1340. In this case, ion conductor 1330 is formed by creating a trench within insulating layer 1340, the trench having a diameter indicated by D2. The trench is then filled using, for example, interference lithography techniques or conformally lining the via with insulating material and using an anisotropic etch process to remove some of the insulating material, leaving a via with a diameter of D3. Structure 1300 formed using this technique may have a ion conductor cross sectional area as small as about 10nm in contact with electrodes 1310 and 1320.

Figures 14-17 illustrate another embodiment of the invention, where the cross sectional area of the ion conductor/electrode interface is relatively small. Structure 1400, illustrated in Figure 14, includes electrodes 1410 and 1420 and an ion conductor 1430. Structure 1400 is formed in a manner similar to structure 700, except that the ion conductor material is deposited conformally, using, for example chemical vapor deposition or physical vapor deposition, into a trench, and the trench is not filled with the ion conductor material.

Structure 1500 is similar to structure 1400, except that an ion conductor 1530 is formed by etching a portion of ion conductor 1430, such that a via 1540 is formed through to electrode 1410. Structure 1600 is similar to structure 1500 and is formed by conformally depositing the ion conductor material as described above and then removing the ion conductor material from a surface of insulating material 1450 prior to depositing electrode 1420 material. Finally, structure 1700 may be formed by selectively depositing the ion conductor 1730 material into only a portion of the trench formed in insulating material 1450 (e.g., using angled deposition and/or shadowing techniques), removing any excess ion conductor material on the surface of insulator 1450, and forming an electrode 1720 overlying the insulator and in contact with ion conductor 1730.

Figures 18 and 19 illustrate yet another embodiment of the invention, where a pillar or wall within a trench is used to reduce a cross-sectional area of the interface between the ion conductor and one or more electrodes. Structure 1800, illustrated in Figure 18, includes electrodes 1810 and 1820 and an ion conductor 1830 formed within an insulating layer 1840.

In addition, structure 1800 includes a pillar 1850 of insulating material (e.g., insulating material used to form layer 1840), formed within a trench within layer 1840. Structure 1800 may be formed using the shadowed deposition technique discussed above. Structure 1900 is similar to structure 1800, except structure 1900 includes a partial pillar 1950 and an ion conductor 1930, which fills the remaining portion of the formed trench.

Figure 20 illustrates yet another structure 2000 in accordance with the present invention. Structure 2000 includes electrodes 2010 and 2020 and an ion conductor 2030 formed within an insulating layer 2040. Structure 2000 is formed using an anisotropic or a combination of an anisotropic and an isotropic etch processes to form a tapered via. Ion conductor 2030 is then formed within the trench using techniques previously described.

Figures 21-24 illustrate programmable devices in accordance with yet another embodiment of the invention. The structures illustrated in Figures 21-24 include a floating electrode, which allows multiple bits of information to be stored within a single programmable device.

Structure 2100 includes a first electrode 2110, a second, floating electrode 2120, a third electrode 2130, ion conductor portions 2140 and 2150, which may all be formed on a substrate or wholly or partially formed within a via as described above. Although structure 2100 is illustrated in a vertical configuration, the structure may be formed in a horizontal configuration, similar to structure 1100. In accordance with one aspect of this embodiment, the first and third electrodes are formed of an indifferent electrode and the second electrode is formed of an oxidizable electrode material. Alternatively, the first and third electrodes may be formed of oxidizable electrode material and the second, floating electrode may be formed of an indifferent electrode material. In either case, the structure includes two "half cells," where each half cell functions as a programmable device described above in connection with Figure 1. Each half cell is preferably configured such that the resistance of one half cell differs from the resistance of the other half cell when both cells are in an erased state.

In the case when floating electrode 2120 is formed of oxidizable electrode material, bits of data may be stored as follows. The overall impedance of structure 2100 is approximately equal to the resistance of portions 2140 and 2150. When no electrodeposit is formed within either portion, this high resistance state may be represent by the state 00. When a voltage is applied to structure 2100, such that electrode 2130 is positive relative to electrode 2110 and the applied bias is greater that the threshold voltage required to form an



electrodeposit in portion 2140, an electrodeposit 2160 will form through conductor portion 2140 from electrode 2110 toward floating electrode 2120 as illustrated in Figure 22. Under this condition, an electrodeposit will not form within conductor portion 2150 because portion 2150 is under a reverse bias condition and thus will not support growth of an electrodeposit.

- 5 The growth of the electrodeposit will change the impedance of portion 2140 from  $Z_1$  to  $Z_1'$ , thus changing the overall impedance of structure 2100, which may be represented by the state 01. The current level used to form electrodeposit 2160 should be selected such that it is sufficiently low, allowing the electrodeposit to be dissolved upon application of a sufficient reverse bias. A third state may be formed by reversing the polarity of the applied bias across
- 10 electrodes 2110 and 2130, such that most of the voltage drop occurs across the high resistance ion conductor portion 2150 and formation of an electrodeposit 2170 begins, as illustrated in Figure 23, without causing electrodeposit 2160 to dissolve. The impedance of portion 2150 changes from  $Z_2$  to  $Z_2'$ , and the overall impedance of structure 2100 is  $Z_1'$  plus  $Z_2'$ , which may be represented by the state 11. Once both half cells are in the write state,
- 15 electrodeposit 2160 and/or 2170 may be dissolved by applying a sufficient bias across one or both of the half cells. Electrodeposit 2170 can be erased, for example, by sufficiently negatively biasing electrode 2130 with respect to electrode 2110, which may be represented by a state 00. The four possible states, along with the current limit used to form the state, are represented in table 1 below.

20

Seq #	Polarity	Current limit	Z half-cell 1	Z half-cell 2	State/value
1	Sub-threshold	Zero	$Z_1$	$Z_2$	00
2	Upper + Lower -	Low	$Z_1'$	$Z_2$	01
3	Upper - Lower +	Low	$Z_1'$	$Z_2'$	11
4	Upper - Lower +	High	$Z_1$	$Z_2'$	10

Table 1

- Structure 2100 can be changed to 11 from state 10 by applying a low current limit
- 25 bias to grow electrodeposit 2150 in portion 2140. Similarly, structure 2100 can be changed from state 11 to state 01 by dissolving electrodeposit 2170 by applying a relatively high current limit bias such that upper electrode 2130 is positive with respect to lower electrode 2110. Finally, structure 2100 can be returned to state 00 using a short current pulse to

thermally dissolve electrodeposit 2160, using a current which is high enough to cause localized heating of the electrodeposit. This will increase the metal concentration in the half-cell but this excess metal can be removed electrically from the cell by plating it back onto the floating electrode. This sequence is summarized in table 2 below.

5

Seq #	Polarity	Current limit	Z half-cell 1	Z half-cell 2	State/value
4	Existing state	-	$Z_1$	$Z_2'$	10
5	Upper + Lower -	Low	$Z_1'$	$Z_2'$	11
6	Upper + Lower -	High	$Z_1'$	$Z_2$	01
7	Upper + Lower -	Thermal	$Z_1$	$Z_2$	00

Table 2

Other write and erase sequences are also possible (as are other definitions of the various states represented by the half-cell impedances). For example, it is possible to go from state 00 to either state 01 or state 10, depending on the write polarity chosen. Similarly, it is possible to go from state 11 to either state 10 or state 01. It is also possible to go from state 11 to state 00 by the application of a current pulse (in either direction) which is high and short enough to thermally dissolve the electrodeposits in both half-cells simultaneously.

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In addition to storing information in digital form, structure 2100 can also be used as a noise-tolerant, low energy anti-fuse element for use in field programmable gate arrays (FPGAs) and field configurable circuits and systems. Most physical anti-fuse technologies require large currents and voltages to make a permanent connection. The need for such high energy state-switching stimuli is generally considered to be somewhat beneficial as this reduces the likelihood of the anti-fuse accidentally forming a connection in electrically noisy situations. However, the use of high voltages and large currents on chip represent a significant problem as all components in the programming circuits are typically sized accordingly and the high energy consumption reduces battery life in portable systems.

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Figures 25-29 illustrate structures in accordance with another embodiment of the invention in which multiple programmable devices include a common electrode (e.g., the devices share a common anode or cathode. Forming structures in which multiple structures

share a common electrode is advantageous because such structures allow a higher density of cells to be formed on a given substrate surface area.

Figures 25 and 26 illustrate a structure 2500, having a horizontal configuration and a common electrode. Structure 2500 includes an electrical connector 2510 coupled to a common surface electrode 2520, electrodes 2530 and 2540, and ion conductor portions 2550 and 2560 overlying an insulating layer 2170. Structure 2500 may be used to form word and bit lines as described above by forming a row of electrodes (e.g., anodes) coupled to conductor 2510, and columns of oppositely bias electrodes (e.g., cathodes) running perpendicular to electrodes 2520. A conductive plug, formed of any suitably conducting material can be used to electrically couple electrode 2520 to conductor 2510. Although illustrated with a horizontal configuration, common electrode structures in accordance with this embodiment may be formed using structures having a vertical configuration as described herein.

Figures 27 and 28 illustrate additional structures 2700 and 2800 having a common electrode shared between two or more devices. Structures 2700 and 2800 include a common electrode, electrodes 2720 and 2725, ion conductors 2730, 2735 and 2830, 2835 respectively, and insulating layers 2740 and 2750. Structures 2700 and 2800 may be formed using techniques described above in connection with Figures 15 and 16—e.g., by conformally depositing ion conductor material within a trench of an insulating layer. In accordance with another embodiment of the invention, directional deposition may be used to form a structure similar to structure 1700. Structures 2700 and 2800 each include two programmable devices including common electrode 2710 an ion conductor (e.g., conductor 2735) and another electrode (e.g., electrode 2725). Dielectric material 2750 is an insulating material that does not interfere with surface electrodeposits growth, such as silicon oxides, silicon nitrides, and the like.

Figure 29 illustrates a structure 2900 including multiple programmable devices 2902-2916 formed about a common electrode 2920. Each of the devices 2902-2916 may be formed using the method described above in connection with Figure 21. In the embodiment illustrated in Figure 29, each of electrodes 2930-2936 and 2938-2944 may be coupled together in a direction perpendicular to the direction of common electrode 2920, such that electrode 2920 forms a bit line and electrodes 2930-2936 and electrodes 2938-2944 form word lines. Structure 2900 may operate and be programmed in a manner similar to structure 2100 described above.

In accordance with other embodiments of the present invention, a programmable structure or device stores information by storing a charge as opposed to growing an electrodeposit. A capacitance of a structure or device is altered by applying a bias across electrodes of the device such that positively charged ions migrate toward one of the electrodes. If the applied bias is less than a write threshold voltage, no short will form between the electrodes. Capacitance of the structure changes as a result of the ion migration. When the applied bias is removed, the metal ions tend to diffuse away from the electrode or a barrier proximate the electrode. However, an interface between an ion conductor and a barrier is generally imperfect and includes defects capable of trapping ions. Thus, at least a portion of ions remain at or proximate an interface between a barrier and an ion conductor. If a write voltage is reversed, the ions may suitably be dispersed away from the interface.

A programmable structure in accordance with the present invention may be used in many applications which would otherwise utilize traditional technologies such as EEPROM, FLASH or DRAM. Advantages provided by the present invention over present memory techniques include, among other things, lower production cost and the ability to use flexible fabrication techniques which are easily adaptable to a variety of applications. The programmable structures of the present invention are especially advantageous in applications where cost is the primary concern, such as smart cards and electronic inventory tags. Also, an ability to form the memory directly on a plastic card is a major advantage in these applications as this is generally not possible with other forms of semiconductor memories.

Further, in accordance with the programmable structures of the present invention, memory elements may be scaled to less than a few square microns in size, the active portion of the device being less than one micron. This provides a significant advantage over traditional semiconductor technologies in which each device and its associated interconnect can take up several tens of square microns.

Additionally, the devices of the present invention require relatively low energy and do not require "refreshing." Thus, the devices are well suitable for portable device applications.

Although the present invention is set forth herein in the context of the appended drawing figures, it should be appreciated that the invention is not limited to the specific form shown. For example, while the programmable structure is conveniently described above in connection with programmable memory devices, the invention is not so limited; the structure of the present invention may suitably be employed as programmable active or passive

devices within a microelectronic circuit. Furthermore, although only some of the devices are illustrated as including buffer, barrier, or transistor components, any of these components may be added to the devices of the present invention. Various other modifications, variations, and enhancements in the design and arrangement of the method and apparatus set forth herein, may be made without departing from the spirit and scope of the present invention as set forth in the appended claims.

**CLAIMS**

We claim:

1. A microelectronic programmable structure comprising:  
5 an ion conductor formed of an ion conductive material and conductive ions;  
an oxidizable electrode proximate the ion conductor; and  
an indifferent electrode proximate the ion conductor.
2. The microelectronic programmable structure of claim 1, further comprising a  
10 buffer layer between the oxidizable electrode and the ion conductor.
3. The microelectronic programmable structure of claim 2, wherein the buffer  
layer comprises a material selected from the group consisting of  $\text{Ag}_x\text{O}$ ,  $\text{Ag}_x\text{S}$ ,  $\text{Ag}_x\text{Se}$ ,  $\text{Ag}_x\text{Te}$ ,  
where  $x \geq 2$ ,  $\text{Ag}_y\text{I}$ , where  $y \geq 1$ ,  $\text{CuI}_2$ ,  $\text{CuO}$ ,  $\text{CuS}$ ,  $\text{CuSe}$ ,  $\text{CuTe}$ ,  $\text{GeO}_2$ , and  $\text{SiO}_2$ .  
15
4. The microelectronic programmable structure of claim 1, wherein the  
indifferent electrode comprises platinum.
5. The microelectronic programmable structure of claim 1, wherein the  
20 oxidizable electrode comprises a material selected from the group consisting of a transition  
metal sulfide and a transition metal selenide.
6. The microelectronic programmable structure of claim 5, wherein the  
oxidizable electrode further comprises intercalated silver.  
25
7. The microelectronic programmable structure of claim 5, wherein the  
oxidizable electrode comprises  $\text{TaS}_2$ .
8. The microelectronic programmable structure of claim 1, wherein the  
30 oxidizable electrode comprises  $\text{AgI}$ .
9. The microelectronic programmable structure of claim 8, wherein the  
oxidizable electrode comprises excess silver.

10. The microelectronic programmable structure of claim 1, wherein the ion conductor comprises a solid solution selected from the group consisting of  $\text{As}_x\text{S}_{1-x}\text{Ag}$ ,  $\text{Ge}_x\text{Se}_{1-x}\text{Ag}$ ,  $\text{Ge}_x\text{S}_{1-x}\text{Ag}$ ,  $\text{As}_x\text{S}_{1-x}\text{Cu}$ ,  $\text{Ge}_x\text{Se}_{1-x}\text{Cu}$ ,  $\text{Ge}_x\text{S}_{1-x}\text{Cu}$ , where x ranges from about 0.1 to about 0.5.

11. The microelectronic programmable structure of claim 10, wherein the ion conductor comprises a filler material.

12. The microelectronic programmable structure of claim 11, wherein the filler material comprises a dielectric and is present in the ion conductor at a volume percent of up to about 50 percent.

13. The microelectronic programmable structure of claim 11, wherein the filler material comprises a dielectric and is present in the ion conductor at a volume percent of up to about 5 percent.

14. The microelectronic programmable structure of claim 11, wherein the filler material comprises silver.

15. The microelectronic programmable structure of claim 1, wherein the ion conductor comprises a glass having a composition of  $\text{Ge}_{0.17}\text{Se}_{0.83}$  to  $\text{Ge}_{0.25}\text{Se}_{0.75}$ .

16. The microelectronic programmable structure of claim 15, wherein the ion conductor further comprises up to about 34 percent silver.

17. The microelectronic programmable structure of claim 1, further comprising a transistor in contact with one of the oxidizable or the indifferent electrodes.

18. The microelectronic programmable structure of claim 1, further comprising a diode in contact with one of the oxidizable or the indifferent electrodes.

19. The microelectronic programmable structure of claim 1, wherein the ion conductor is formed within a via in an insulating material layer.

20. The microelectronic programmable structure of claim 19, further comprising  
5 a diode formed within the via.

21. The microelectronic programmable structure of claim 19, wherein the ion conductor contacts the indifferent electrode about a portion of the perimeter of the ion conductor.  
10

22. The microelectronic programmable structure of claim 21, wherein the ion conductor contacts the indifferent electrode about a sloped portion of the perimeter of the ion conductor.

23. The microelectronic programmable structure of claim 1, wherein the indifferent electrode, the oxidizable electrode, and the ion conductor are formed on a surface of an insulating material layer.  
15

24. The microelectronic programmable structure of claim 1, wherein the ion conductor is formed within a via of a first insulating material layer, and wherein the programmable structure further comprises a second insulating material formed within the via.  
20

25. The microelectronic programmable structure of claim 1, wherein the ion conductor is formed along a sidewall of a via formed within an insulating layer.  
25

26. The microelectronic programmable structure of claim 1, wherein the ion conductor is formed within a sloped via within an insulating material layer.

27. The microelectronic programmable structure of claim 1, further comprising a barrier layer between the indifferent electrode and the ion conductor.  
30



28. The microelectronic programmable structure of claim 27, wherein the barrier layer comprises a conductive material.

29. The microelectronic programmable structure of claim 27, wherein the barrier layer comprises an insulating material.

30. The microelectronic programmable structure of claim 1, wherein surface area of the indifferent electrode in contact with the ion conductor is less than the surface area of the oxidizable electrode in contact with the ion conductor.

31. The microelectronic programmable structure of claim 1, wherein an interface between the indifferent electrode and the ion conductor is roughened.

32. A multi-cell programmable microelectronic device comprising:  
a first electrode of a first type;  
a second electrode of a second type;  
a first ion conductive material of a first resistance interposed between the first electrode and the second electrode;  
a third electrode of a first type; and  
a second ion conductive material of a second resistance interposed between the second electrode and the third electrode.

33. The multi-cell programmable microelectronic device of claim 32, wherein the first and third electrodes comprise an indifferent electrode material and the second electrode comprises an oxidizable electrode material.

34. The multi-cell programmable microelectronic device of claim 32, wherein the first and third electrodes comprise an oxidizable electrode material and the second electrode comprises an indifferent electrode material.

35. A multi-cell programmable microelectronic device comprising:  
a plurality of electrodes of a first type;  
a plurality of electrodes of a second type; and

a plurality of ion conductor structures, wherein at least one of the plurality of ion conductor structures is interposed between one of the plurality of electrodes of a first type and one of the plurality of electrodes of a second type, and

5 wherein a plurality of electrodes of a first type are electrically coupled together.

36. The multi-cell programmable microelectronic device of claim 35, wherein the plurality of electrodes of a first type comprise oxidizable electrode material.

10 37. The multi-cell programmable microelectronic device of claim 35, wherein the plurality of electrodes of a first type comprise indifferent electrode material.

38. The multi-cell programmable microelectronic device of claim 35, wherein at least a portion of the plurality of ion conductor structures are formed within a via within an  
15 insulating material layer.

39. The multi-cell programmable microelectronic device of claim 35, wherein at least a portion of the plurality of ion conductor structures are formed on a surface of an insulating material layer.

20 40. A method of forming a programmable microelectronic structure, the method comprising the steps of:

providing a substrate;  
forming a layer of electrode material of a first type overlying the substrate;  
25 forming an insulating layer overlying the layer of electrode material of a first type;  
forming a via through the insulating layer and the layer of electrode material of a first type;  
depositing ion conductor material into the via; and  
30 forming an electrode of a second type overlying the ion conductor material.

41. The method of claim 40, wherein the step of forming a via includes isotropically etching the insulating layer.

42. The method of claim 40, wherein the step of forming a via includes anisotropically etching the insulating layer.

5 43. The method of claim 40, wherein the step of forming a via includes isotropically etching the layer of electrode material of a first type.

44. The method of claim 40, wherein the step of forming a via includes anisotropically etching the layer of electrode material of a first type.

10

45. The method of claim 40, further comprising the step of applying a bias across the electrode material of the first type and the electrode material of the second type to manipulate a concentration of conductive material in the ion conductor.

15

46. The method of claim 40, further comprising the step of applying a bias across the electrode material of the first type and the electrode material of the second type to manipulate an amount of conductive material present in one of the electrode material of the first type and the electrode material of the second type.

20

47. The method of claim 40, wherein the step of depositing ion conductor material comprises depositing germanium onto a surface and reacting the germanium with  $H_2Se$ .

25

48. The method of claim 40, wherein the step of depositing ion conductor material comprises depositing arsenic onto a surface and reacting the arsenic with  $H_2Se$ .

30

49. The method of claim 40, wherein the step of depositing ion conductor material comprises depositing germanium onto a surface and reacting the germanium with  $H_2S$ .

50. The method of claim 40, wherein the step of depositing ion conductor material comprises depositing arsenic onto a surface and reacting the arsenic with  $H_2S$ .

51. A method of forming a programmable microelectronic device, the method comprising the steps of:

forming an ion conductor structure overlying a substrate;

depositing an electrode material layer overlying the ion conductor structure;

5 and

patterning the electrode material layer to form electrodes in contact with the ion conductor structure.

52. The method of claim 51, wherein the step of forming an ion conductor structure comprises depositing germanium onto a surface and reacting the germanium with  $H_2Se$ .

53. A method of forming an electronic device, the method comprising the steps of:

15

forming a first electrode on a surface of a substrate;

depositing a first insulating layer over a surface of a the first electrode;

forming a via in the first insulating layer;

depositing a second insulating material within a portion of the via;

depositing ion conductor material within a portion of the via; and

20

forming a second electrode overlying the ion conductor.

54. The method of forming an electronic device of claim 53, wherein the step of depositing ion conductor material comprises the step of depositing the ion conductor material within a via formed in the second insulating material.

25

55. The method of forming an electronic device of claim 53, wherein the step of depositing a second insulating material comprises using a directional deposition technique.

56. The method of forming an electronic device of claim 53, wherein the step of depositing an ion conductor material comprises forming a conformal layer of ion conductor material.

30

57. The method of forming an electronic device of claim 53, further comprising the step of removing a portion of the ion conductor material from a surface of the first insulating material.

5 58. A method of forming a multi-cell programmable device, the method comprising the steps of:

forming a first electrode on a surface of a substrate;  
forming a first ion conductor portion overlying the first electrode;  
forming a second electrode overlying the first ion conductor portion;  
10 forming a second ion conductor portion overlying the second electrode; and  
forming a third electrode overlying the second ion conductor portion.

59. A method of forming a glass composition, the method comprising the steps of:

15 selecting an ampoule;  
cleaning the ampoule using hydrofluoric acid;  
drying the ampoule for about 24 to about 120 hours at about 120 °C;  
evacuating the ampoule;  
heating the ampoule until the ampoule turns red;  
20 filling the ampoule with a charge;  
heating the ampoule to a temperature below the melting temperature of the glass constituents;  
ramping the temperature at a rate of about 0.5 degrees per minute to a temperature about 50 °C higher than the liquidus temperature of the glass; and  
25 slow rocking the glass composition at a rate of about 20 per minute for a period of about six hours.

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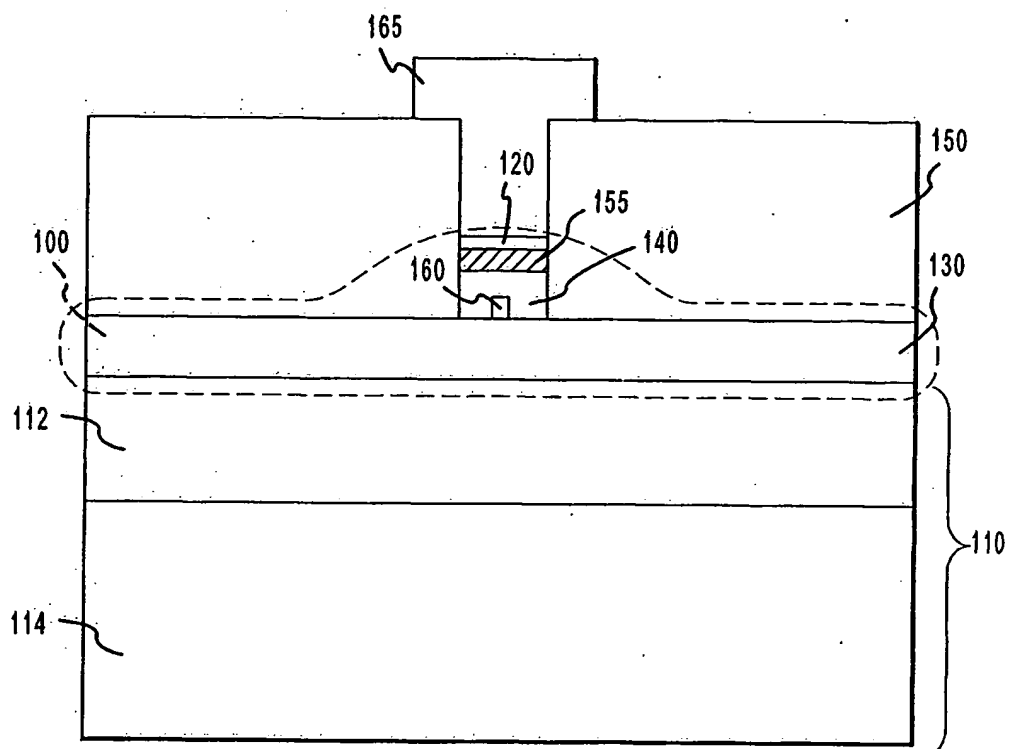


FIG.1

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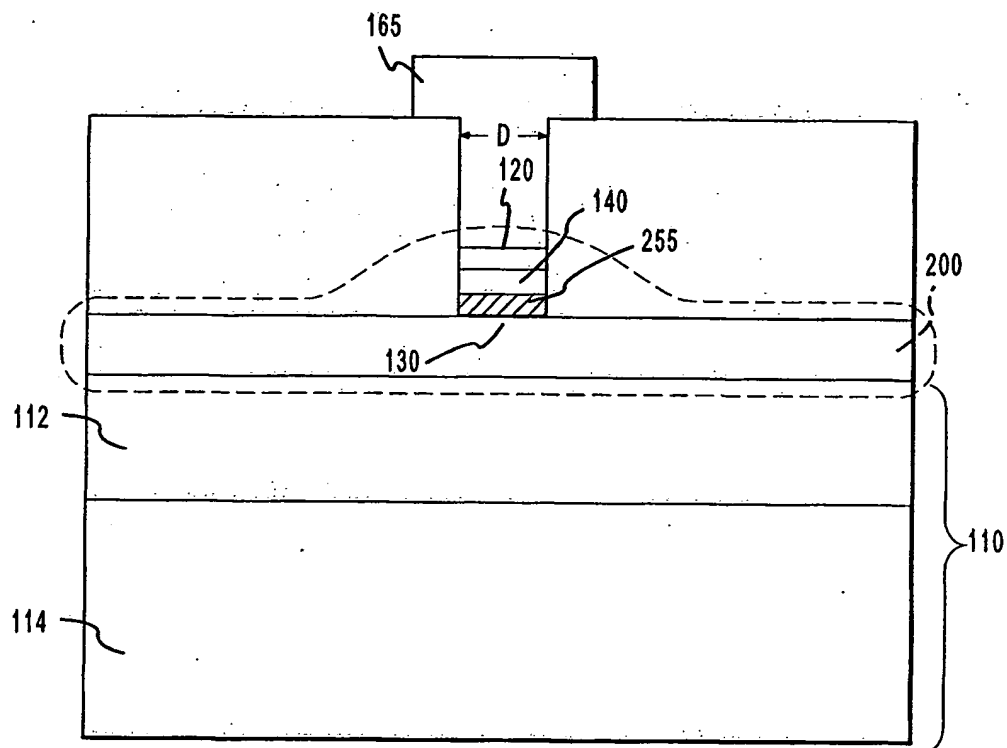


FIG.2

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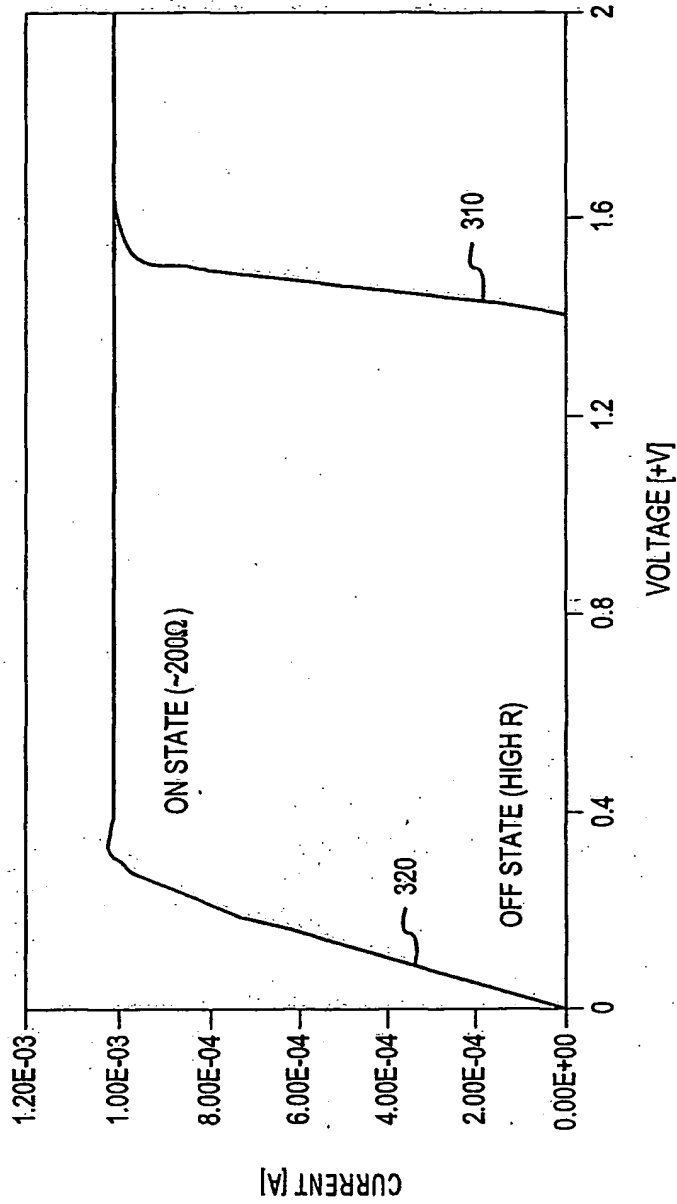


FIG.3



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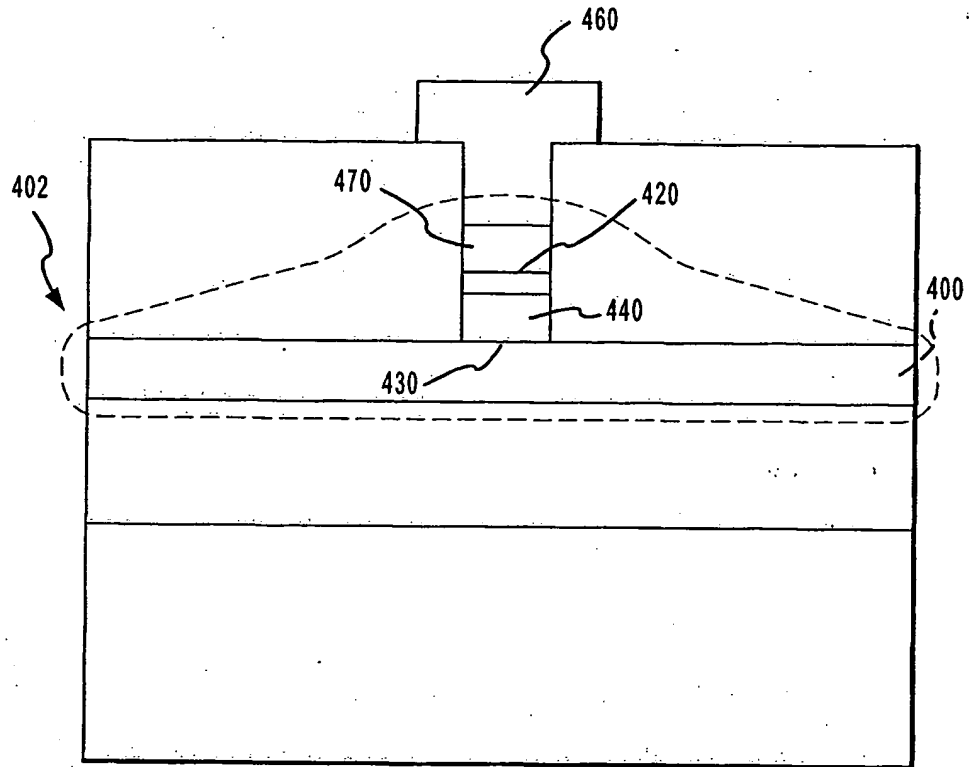


FIG.4

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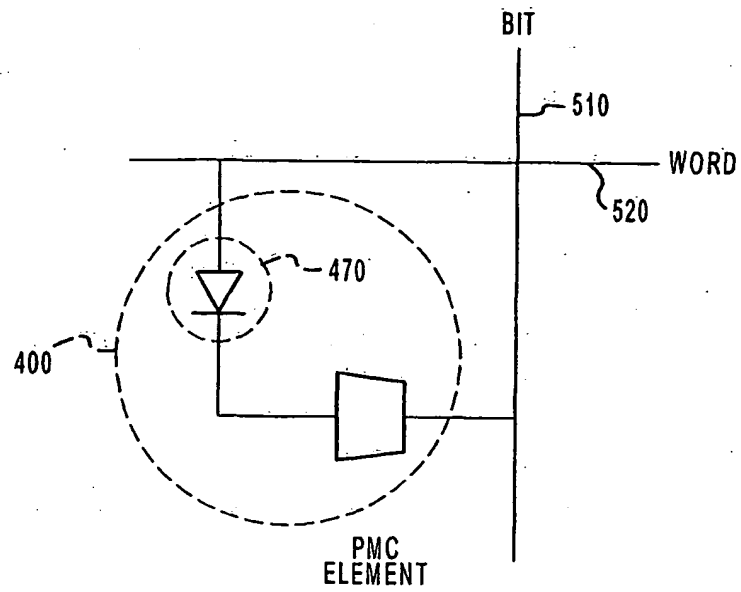


FIG.5

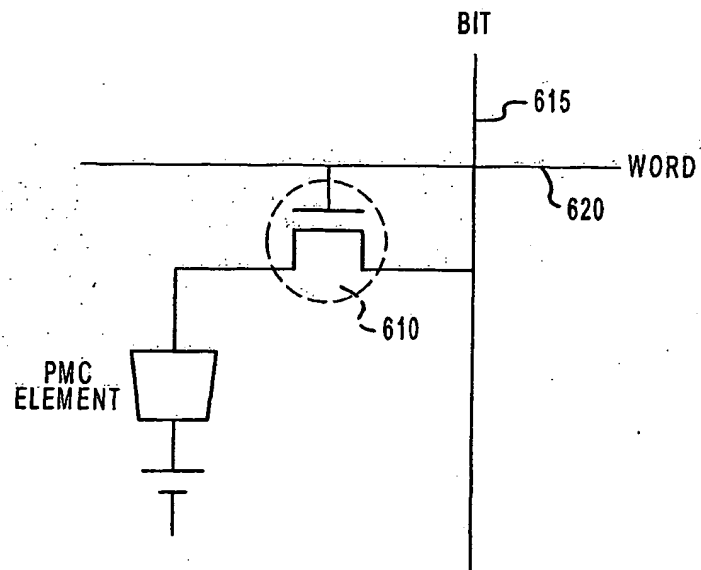


FIG.6

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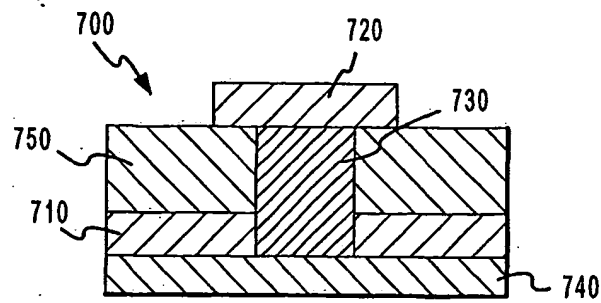


FIG.7

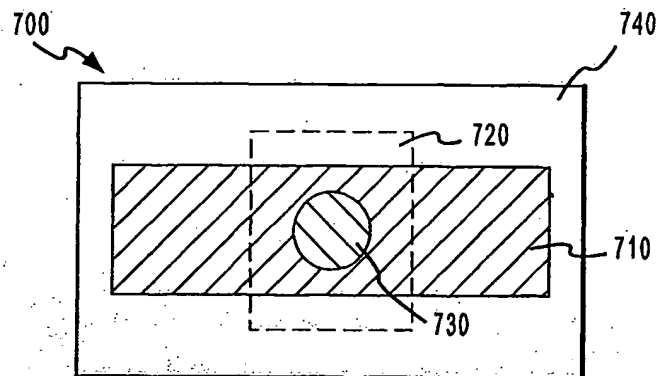


FIG.8

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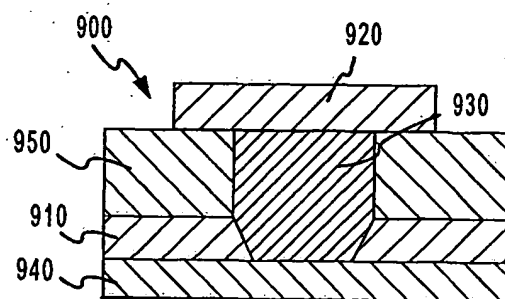


FIG.9

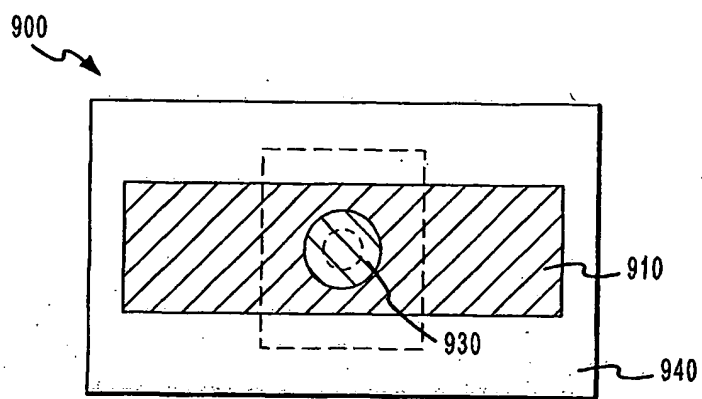


FIG.10

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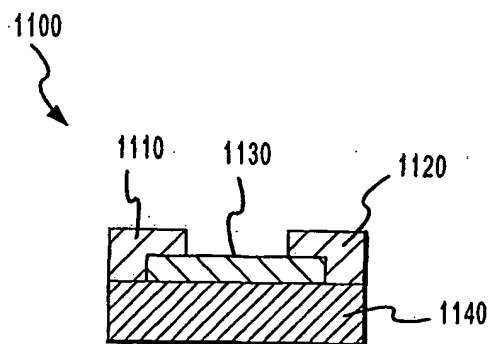


FIG. 11

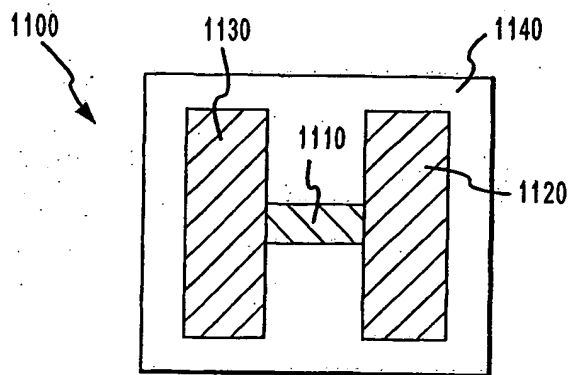


FIG. 12

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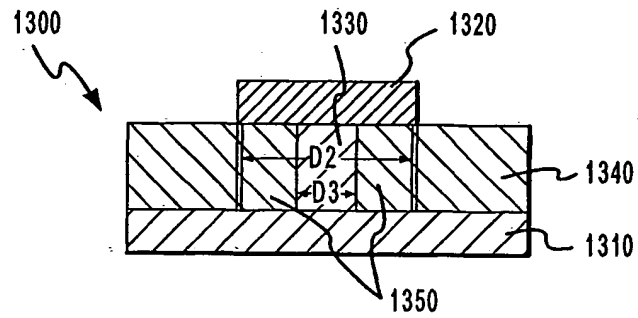


FIG. 13

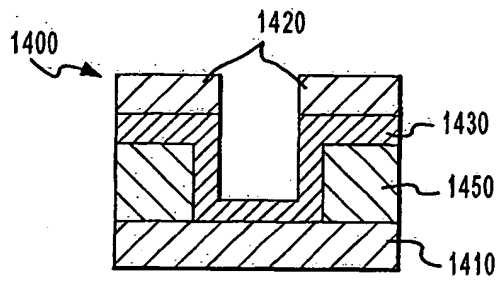


FIG. 14

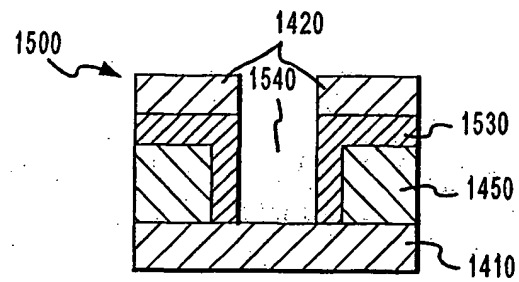


FIG. 15

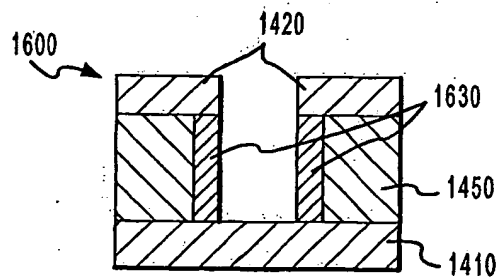


FIG. 16

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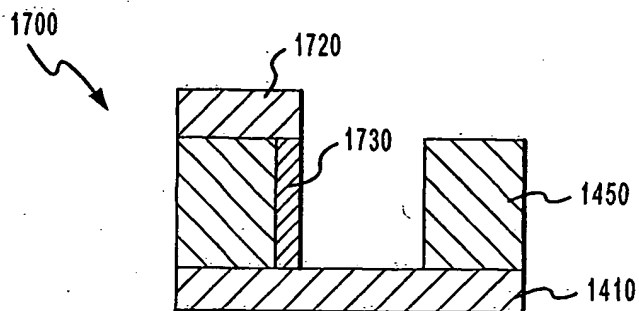


FIG. 17

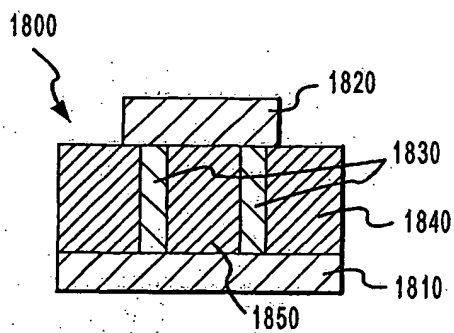


FIG. 18

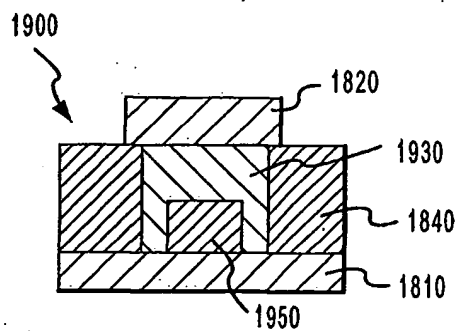


FIG. 19

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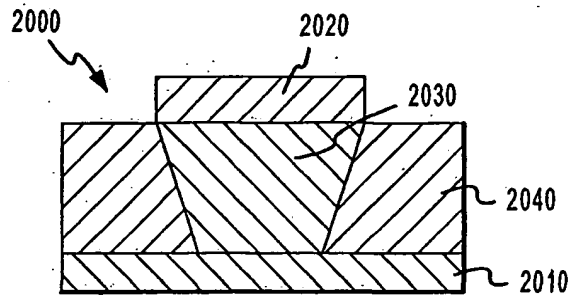


FIG. 20

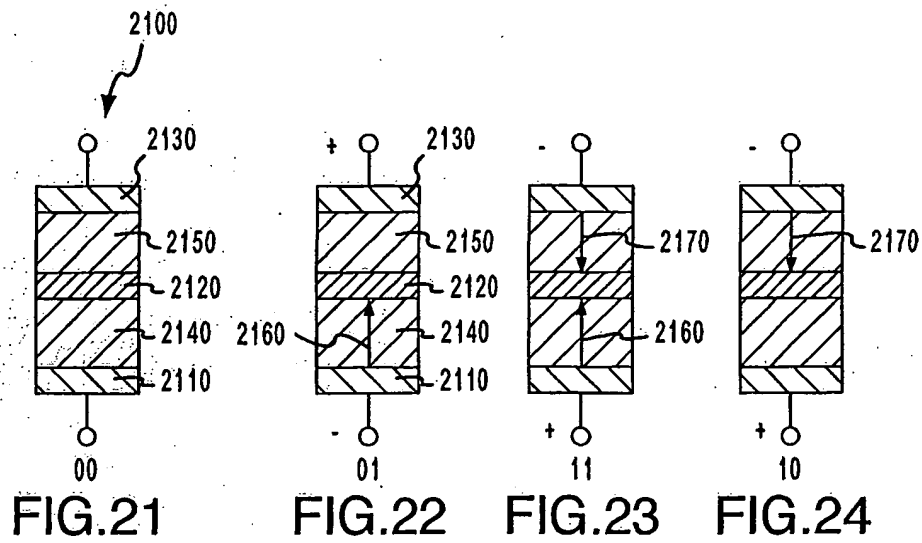


FIG. 21

FIG. 22

FIG. 23

FIG. 24



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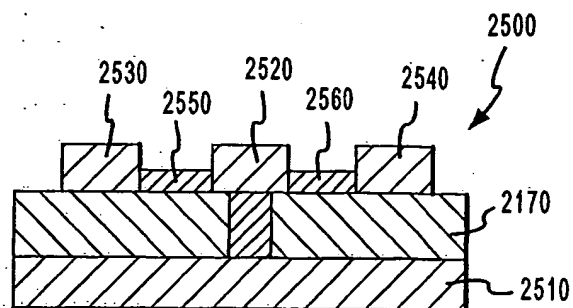


FIG.25

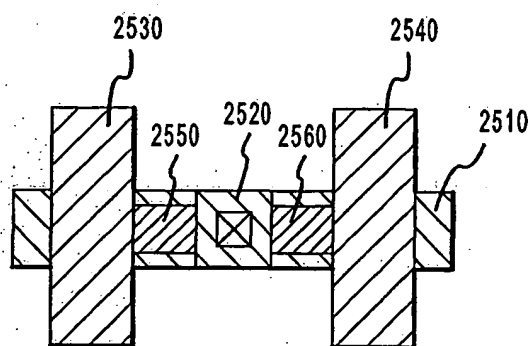


FIG.26

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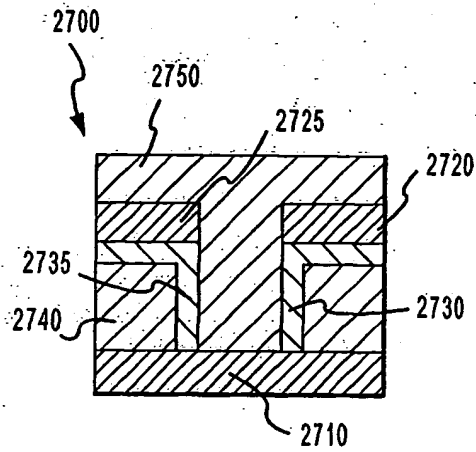


FIG. 27

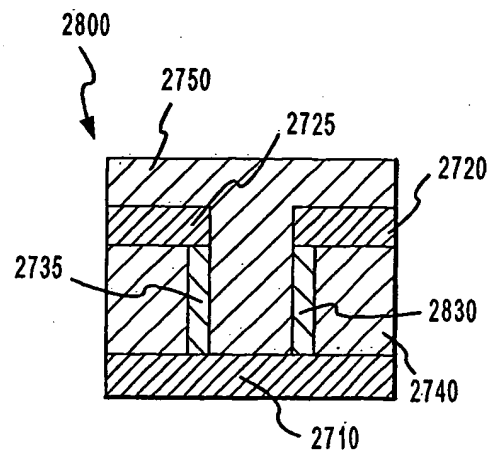


FIG. 28

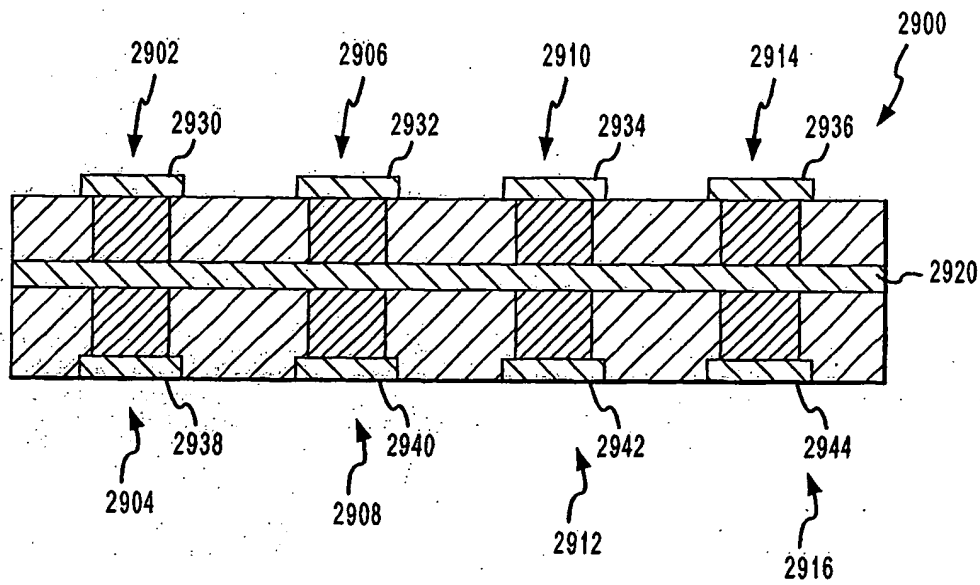


FIG. 29

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/28266

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(7) : H01C 7/00 US CL : 338/13,20,80; 257/57; 365/153; 501/40 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 338/13,20,80; 257/57; 365/153 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EAST		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,084,796 A (KOZICKI et al) 04 July 2000 (04.07.2000), col. 2, lines 30-50; col. 3, lines 25-46; cols. 5-6; col. 9; cols. 10, line 60 - col. 11, line 6; and Figs. 5D, 6B.	1-19,21-46,51-58
X	US 5,846,889 A (HARBISON et al) 08 December 1998 (08.12.1998), col. 4, lines 3-15 and col. 5, lines 1-31.	59
X	US 5,315,131 A (KISHIMOTO et al) 24 May 1994 (24.05.1994), col. 3, lines 1-26; col. 5, lines 1-47; and Figs. 1-3.	1-3,11,12,17,18,23,27-29,31,35-37,39,51
X	US 4,419,421 A (WICHELHAUS et al) 06 December 1983 (06.12.1983), Fig. 2.	1,3
A	US 4,499,557 A (HOLMBERG et al) 12 February 1985 (12.02.1985), whole document.	1-58
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	documents which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search 07 November 2001 (07.11.2001)		Date of mailing of the international search report 31 DEC 2001
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer KARL EASTHOM Telephone No. (703) 308-0956 <i>Renée Proulx</i>

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/28266

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:  
Please See Continuation Sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☐

No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/28266

### BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

Group I, claims 1-31, drawn to a microelectronic programmable structure having an ion conductive material, and oxidizable and indifferent electrodes

Group II, claims 32-39 and 58 drawn to a multi-cell programmable device and method of forming thereof, and having or forming three electrodes and two ion conductive materials.

Group III, claims 40-52 drawn to two methods of forming a programmable structure - by forming a via and depositing ion conductive material; by patterning electrodes and using ion conductive material.

Group IV, claims 53-57, drawn to a method of forming an electronic device.

Group V, claim 59, drawn to a method of forming a glass composition.

The reasons are that there are no corresponding technical features linking the inventions. Group V is directed to forming a glass composition; Group IV is drawn to forming an electronic device, Group III is drawn to several methods of forming programmable structure, Group II is directed to a multi-cell programmable devices, and Group I is directed to microelectronic programmable structure having an oxidizable and an indifferent electrode, and an ion conductor.